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SUPPORTED COBALT CATALYSTS – PREPARATION, CHARACTERISATION AND REACTION STUDIES

Doctoral Dissertation

Leif Backman

Helsinki University of Technology
Faculty of Chemistry and Materials Sciences
Department of Biotechnology and Chemical Technology

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Abstract

The aim of this work was to understand on the effect of thermal treatments, precursor and support on the interaction between the support and cobalt species, and further how the interaction affects the reducibility and dispersion of the catalyst. Silica and alumina supported cobalt catalysts were prepared, characterised and tested for catalytic activity. The catalysts were prepared by gas phase deposition techniques from cobalt acetylacetonate and cobalt carbonyl and by incipient wetness impregnation from cobalt nitrate.

One of the goals was to investigate whether atomic layer deposition (ALD) using cobalt acetylacetonate precursors can produce well dispersed reducible cobalt catalysts. The cobalt acetylacetonates, $Co(acac)_2$ and $Co(acac)_3$, were found suitable for ALD. Silica supported catalysts were prepared by chemisorption of $Co(acac)_3$, while $Co(acac)_2$ was used on alumina. The main mode of interaction on silica was the ligand exchange reaction with OH groups. On alumina both the ligand exchange reaction and dissociative adsorption occurred. Steric hindrance limited the amount of precursor on the support. The acac ligands were removed through calcination at 450 °C. The cobalt loading was increased by repeating the precursor addition and air calcination steps up to five times; samples with about 2 to 8 Co atoms per nm^2 were achieved on both silica and alumina.

Calcination of the cobalt acetylacetonate modified samples led to the formation of silicate- or aluminate-type species, which decreased the reducibility of the catalysts. The reducibility was enhanced when the calcination step after the last precursor reaction step was omitted ('uncalcined' catalysts). High reduction temperatures were still needed: the maximum metal surface area was obtained after reduction at 500–600 °C. The cobalt dispersion on the uncalcined ALD catalysts was, in general, higher than on the calcined catalysts. Furthermore, the dispersion was higher on the alumina supported catalysts than on corresponding silica supported ones.

The interaction between cobalt and silica on the nitrate based catalysts was found to be weak, which led to high reducibility but modest dispersion. The main cobalt species on the catalysts was Co_3O_4. The use of reduction temperatures above 400 °C induced sintering or migration of silica, which decreased the cobalt surface area significantly.

Dicobalt octacarbonyl, $Co_2(CO)_8$, was adsorbed on silica by vapour-phase adsorption in a fluidised bed reactor under CO. The carbonyl interacted through hydrogen bonding and rearranged to $Co_4(CO)_{12}$ on the support. The amount of precursor that adsorbed on the support was limited by steric hindrance. Decarbonylation was achieved by heat treatment, and higher cobalt loadings were obtained by repeating the deposition and decarbonylation steps.

Chemisorption of hydrogen on cobalt was found to be activated and highly reversible. The effect was stronger on alumina than on silica supported samples. The ALD and nitrate based catalysts were tested for gas phase hydrogenation of toluene, and the activity was found to correlate with the available surface area of metallic cobalt.

Keywords Cobalt catalysts, Cobalt acetylacetonate, Reducibility, Dispersion, Hydrogenation, ALD

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Sammanfattning (Abstrakt)

Grunden för detta arbete var att förstå hur reducibiliteten och dispersionen påverkas av termiska behandlingar, prekursorer och bärare. Kiseloxid (silika) och aluminiumoxid (alumina) burna kobolt katalysatorer tillverkades och deras egenskaper och katalytiska aktivitet undersöktes. Katalysatorerna tillverkades med gasfas metoder genom att använda koboltacetylacetonat och koboltkarbonyl prekursorer, samt genom impregnering med koboltnitrat.

Ett av målen var att undersöka om atomskiktsdeposition (ALD) med koboltacetylacetonat prekursorer ger reducerbara katalysatorer med hög dispersion. Koboltacetylacetonat föreningar, $Co(acac)_2$ och $Co(acac)_3$, visades vara lämpliga för tillverkning av katalysatorer genom ALD. Katalysatorer med silika bärare tillverkades med $Co(acac)_3$ som prekursor, medan $Co(acac)_2$ användes på alumina. Den huvudsakliga reaktionen var ligandutbyte med OH grupper på bäraren. På alumina förekom både ligandutbyte och dissociativ adsorption. Mängden prekursor som reagerade med bäraren fanns vara steriskt begränsad. Acac-liganderna avlägsnades genom kalcinering vid 450°C. Kobolt koncentrationen kunde ökas genom att repetera prekursor adsorption och kalcinerings sekvensen upp till fem gånger, detta gav 5–20 vikt-% Co på silika och 3–10 vikt-% Co på alumina. Detta motsvarade en ökning av ytkoncentrationen av kobolt från ca. 2 to 8 Co atomer per nm^2 på både silika och alumina.

Kalcineringen av ALD katalysatorerna ledde till koboltsilikat och -aluminat liknande föreningar som försämrade reducerbarheten. Reducerbarheten förbättrades när kalcineringen utlämnades efter den sista prekursor reaktions sekvensen (‘icke kalcinerad’ katalysator). Höga reduktionstemperaturer behövdes ändå, då den största metall ytarean erhölls vid reduktion i 500–600°C. Dispersionen var i allmänhet bättre på de icke kalcinerade ALD katalysatorerna än på motsvarande kalcinerade katalysatorer. Alumina bärare gav en bättre dispersion än på silika.

Den svaga samverkan mellan kobolt och silika på de nitratbaserade katalysatorerna ledde till en god reducerbarhet men en dålig dispersion. På dessa katalysatorer förekom främst koboltoxid (Co_3O_4). Användningen av reduktionstemperaturer över 400°C ledde till en kraftigt minskande kobolt ytarea.

Dikoboltoktakarbonyl, $Co_2(CO)_8$, adsorberades på silika från gasfasen under kolmonoxid. Koboltkarbonylen samverkade med bärarens OH grupper genom vätebindning och omorganiserades till $Co_4(CO)_{12}$ på bäraren. Mängden prekursor som kunde adsorberas var steriskt begränsad. Karbonylen kunde sönderdelas genom värmebehandling, och högre koboltkoncentrationer erhölls genom att repetera adsorptions och sönderdelnings sekvenserna.

Kemisorptionen av väte på kobolt fanns vara en aktiverad process. Effekten fanns vara kraftigare på katalysatorer med alumina än med silika bärare. Den katalytiska aktiviteten för gas fas hydrering av toluen hos några ALD och nitratbaserade katalysatorer undersöktes. Aktiviteten fanns korrelera med ytarean av metallisk kobolt.

Ämnesord (Nyckelord) kobolt katalysatorer, koboltacetylacetonat, reducibilitet, dispersion, hydrering, ALD

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PREFACE

The practical work for this thesis was carried out in the Laboratory of Industrial Chemistry at the Helsinki University of Technology between February 1995 and April 2001. The ALD catalysts were prepared at Microchemistry Ltd (former subsidiary of Neste Oil Corp.) and the carbonyl based samples were prepared at the University of Joensuu.

The funding from the Academy of Finland and the Nordic Ministry Council is gratefully acknowledged. Sincere thanks also go to the organisers and participants of the Graduate School in Chemical Engineering (GSCE) for the opportunity to participate in courses and for the good spirit that prevailed within the GSCE.

I especially wish to thank my supervisor, Professor Outi Krause, for her valued support and advice over the years, and for always taking a positive attitude towards my work. I wish also to express my gratitude to my co-authors, especially Marina Lindblad, Aimo Rautiainen, Marita Niemelä, Riikka Puurunen, Sari Suvanto and Olli Jylhä, for their efforts. All the experimental work done by undergraduate students and summer trainees over the years is also appreciated. Colleagues and staff of the laboratories of Industrial Chemistry and Polymer Technology are thanked for the relaxed and enjoyable working atmosphere.

My professional interests turned towards atmospheric chemistry and climate in 2001 when I joined the Finnish Meteorological Institute. All members of the former ozone and UV group, then led by Prof. Petteri Taalas, are thanked for providing a stimulating environment. Thanks go to all co-workers at FMI, and especially I want to thank Juhani Damski, Laura Thölix and Prof. Esko Kyrö for being more than co-workers. I am grateful to Prof. Jarkko Koskinen, Johanna Tamminen and Prof. Gerrit de Leeuw for encouraging me to finalise my thesis and to Prof. Yrjö Viisanen, Prof. Ari Laaksonen and Prof. Markku Kulmala for providing me the opportunity to wrap-up this thesis.

Friends and family made a special contribution in providing all those good things outside work.

Helsingfors, December 2008
Leif Backman

LIST OF APPENDED PUBLICATIONS

This thesis is based on the following seven appended publications [**I**–**VII**]:

I M.K. Niemelä, L. Backman, A.O.I. Krause and T. Vaara, The activity of the Co/SiO_2 catalyst in relation to pretreatment, *Appl. Catal. A* **156** (1997) 319–334.

II A. Rautiainen, M. Lindblad, L.B. Backman and R.L. Puurunen, Preparation of silica-supported cobalt catalysts through chemisorption of cobalt(II) and cobalt(III) acetylacetonate, *Phys. Chem. Chem. Phys.* **4** (2002) 2466–2472.

III L.B. Backman, A.O. Rautiainen, M. Lindblad, O. Jylhä and A.O.I. Krause, Characterisation of Co/SiO_2 catalysts prepared from $Co(acac)_3$ by gas phase deposition, *Appl. Catal. A* **208** (2001) 223–234.

IV L.B. Backman, A. Rautiainen, A.O.I. Krause and M. Lindblad, A novel Co/SiO_2 catalyst for hydrogenation, *Catal. Today* **43** (1998) 11–19.

V S. Suvanto, T.A. Pakkanen and L. Backman, Controlled deposition of $Co_2(CO)_8$ on silica in a fluidized bed reactor: IR, chemisorption and decomposition studies, *Appl. Catal. A* **177** (1999) 25–36.

VI L.B. Backman, A. Rautiainen, M. Lindblad and A.O.I. Krause, Effect of support and calcination on the properties of cobalt catalysts prepared by gas phase deposition, *Appl. Catal. A* **191** (2000) 55–68.

VII L.B. Backman, A. Rautiainen, M. Lindblad and A.O.I. Krause, The interaction of cobalt species with alumina on Co/Al_2O_3 catalysts prepared by atomic layer deposition, *Appl. Catal. A* **360** (2009) 183–191.

Contribution of the author to the appended papers:

I The author contributed to the research plan, carried out a significant part of the chemisorption measurements and some of the reaction experiments (toluene hydrogenation), participated in the interpretation of the results and contributed to the manuscript.

II The author participated in the interpretation of some of the results and in the preparation of the manuscript.

III The author drew-up the research plan to characterise the samples, carried out the chemisorption, physisorption and reaction experiments, interpreted the results and wrote the manuscript together with the co-authors.

IV The author drew-up the research plan to characterise the samples, prepared some of the samples (impregnated catalysts), carried out the chemisorption, oxygen titration and TPR measurements as well as the reaction experiments, interpreted the results and wrote the manuscript together with the co-authors.

V The author did the measurements, interpretation and writing of the hydrogen chemisorption and TPR studies.

VI The author drew-up the research plan to characterise the samples, carried out the chemisorption and reducibility studies and the temperature programmed studies, interpreted the results and wrote the manuscript together with the co-authors.

VII The author drew-up the research plan to characterise the samples, carried out the chemisorption, reducibility and reaction studies, interpreted the results and wrote the manuscript together with the co-authors.

SUPPORTED COBALT CATALYSTS—PREPARATION, CHARACTERISATION AND REACTION STUDIES

Leif Backman

CONTENTS

ABBREVIATIONS

Catalysts

The various catalyst samples are designated in the text as follows:
[wt.% Co]-Co([precursor],[treatment])/[precalcination temperature (°C)]-[support]

[precursor]	N	Cobalt nitrate, $Co(NO_3)_2 \cdot 6H_2O$
	A2	Cobalt(II)acetylacetonate, $Co(acac)_2$
	A3	Cobalt(III)acetylacetonate, $Co(acac)_3$
	C	Cobalt octacarbonyl, $Co_2(CO)_8$
[treatment]	C	calcined
	U	uncalcined (not decarbonylated)
	D	decarbonylated
[support]	SiO_2	silica
	Al_2O_3	alumina

For example,

6.3-Co(A2,U)/875-Al_2O_3	6.3 wt.% Co, Cobalt(II)acetylacetonate precursor, uncalcined, alumina support precalcined at 875 °C
Co(C,D)/400-SiO_2	Cobalt octacarbonyl precursor, decarbonylated, silica support precalcined at 400 °C
Co(N,C)/SiO_2	Cobalt nitrate precursor, calcined, silica support

Abbreviations list

AAS	Atomic absorption spectrometry
ALD	Atomic layer deposition
ALE	Atomic layer epitaxy
a.u.	Arbitrary units
BET	Brunauer-Emmett-Teller
CVD	Chemical vapour deposition
DRIFTS	Diffuse reflectance infrared Fourier transform spectroscopy
DTA	Differential thermal analysis
ICP-MS	Inductively coupled plasma mass spectrometry
INAA	Instrumental neutron activation analysis
IR	Infrared
^{1}H MAS NMR	^{1}H Magic Angle Spinning Nuclear Magnetic Resonance
SEM/EDS	Scanning electron microscope/Energy dispersive spectrometer
TCD	Thermal conductivity detector
TEM	Transmission electron microscopy
TG/DTG	Thermogravimetry/Differential thermal analysis
TOF	Turnover frequency
TPD	Temperature programmed desorption
TPR	Temperature programmed reduction
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Compounds

acac	Acetylacetonate (ligand)
Al_2O_3	Alumina, aluminium oxide
$Al(acac)_3$	Aluminium acetylacetonate
$Co(acac)_2$	Cobalt(II) acetylacetonate
$Co(acac)_3$	Cobalt(III) acetylacetonate
$Co_2(CO)_8$	Dicobalt octacarbonyl
$Co(NO_3)_2 \cdot 6H_2O$	Cobalt nitrate hexahydrate
H(acac)	Acetylacetone
SiO_2	Silica, silicon dioxide
TiO_2	Titanium dioxide

1 INTRODUCTION

1.1 Supported cobalt catalysts

1.1.1 Cobalt–support interaction: reducibility and dispersion

The function of the support is to enable the formation of a well-dispersed catalytically active phase. Typically, porous oxides such as Al_2O_3, SiO_2 and TiO_2 are used. The available active surface area for a given amount of catalytic material will depend on the dispersion, i.e., the ratio of exposed to the total amount of metal. However, the interaction at the interface between the dispersed active material and the support can lead to new compounds or strongly interacting oxide phases, which may alter the properties of the catalyst. A weaker interaction gives larger particles and higher reducibility, and a stronger interaction smaller particles and lower reducibility [e.g. 1,2]. In addition to the support material, the interaction is strongly dependent on the precursor, the preparation method, thermal treatment (drying, calcination), metal content and activation conditions. All these parameters will therefore also affect the particle size and reducibility of the catalyst.

A wide range of studies have been published on the interaction between metal and support on silica and alumina supported cobalt catalysts. In general, the formation of poorly reducible cobalt surface species is less common on silica than on alumina [1,3,4]. However, it has been reported that silica supported cobalt in some cases can form poorly reducible silicate-type compounds, for example during high temperature calcination [5–7], due to hydrothermal treatment [8], through reaction between CoO and silica during reduction [9], and following decomposition of cobalt nitrate in vacuum [10]. Alumina supported cobalt readily forms poorly reducible aluminate-type species [11–15] or a cobalt oxide phase that interacts strongly with the support [1,16]. The degree of reduction has been found to decrease with decreasing cobalt crystallite size for particles below ca. 15 nm on Al_2O_3, SiO_2 and TiO_2, due to increasing metal-support interaction [1]. Production of a well-dispersed cobalt phase without the formation of large fractions of nonreducible cobalt species poses a difficult challenge.

The Fischer–Tropsch synthesis, i.e., catalytic hydrogenation of CO, provides a way to convert a carbon source, such as coal, natural gas or biomass, to liquid fuels and chemicals [17–19]. Of the metals that are active in the Fischer–Tropsch synthesis, cobalt and iron are the preferred ones, due to selectivity and cost reasons [17–19]. Both cobalt and iron based catalysts are currently used commercially for the synthesis of hydrocarbons from natural gas and coal [18,19]. Because cobalt is hundreds of times more expensive than iron, the available surface area needs to be optimised [18].

Recent concerns about environmental issues, especially climate change due to increasing atmospheric concentrations of greenhouse gases [20], have led to demands for the development of sustainable fuel technologies. An increased interest towards alternative fuels or biofuels has been triggered as a result. The production of biofuels through catalytic conversion of bio-syngas provides one route [e.g. 21,22].

Activity in the Fischer–Tropsch reaction is independent of the cobalt particle size, i.e., it is proportional only to the area of the metal surface, at least for particle sizes above 8 nm [23]. However, both activity and selectivity are influenced by the particle size at high dispersion [23–29]. The specific activity decreases with particle size for particle sizes below 6–8 nm shown for carbon nanofiber supported catalyst [29]. Furthermore, the deactivation involving reoxidation of cobalt by water in CO hydrogenation occurs preferably on small particles [30–33]. Reoxidation by water might not, however be a major deactivation mechanism under normal Fischer–Tropsch conditions [34]. The degree of reduction can also influence the selectivity: with decreasing extent of reduction the selectivity for shorter hydrocarbons increases [30].

In addition to optimising the reducibility and the particle size, one also needs to consider effects related, for example, to promoters and support properties. The pore diameter of the support has been shown to determine the cobalt particle size on impregnated catalysts [33,35] and can therefore influence catalyst properties. Furthermore, isomerisation and other secondary reactions on the support can affect the selectivity [36].

1.1.2 Catalyst preparation by atomic layer deposition

The need to better control the catalyst dispersion and composition has led to the use of new preparation methods, including a variety of chemical vapour deposition (CVD) techniques. These methods have some advantages over traditional impregnation methods. There is no interference of the solvent in gas phase impregnation techniques and there is no need for a drying step. Any hazardous waste from the solvent is also eliminated. These methods may also offer a better control of the precursor adsorption process.

Atomic layer deposition (ALD, previously known as atomic layer epitaxy, ALE) is a CVD technique based on saturating chemisorption of the precursor on the support [37]. The reactants must be sufficiently volatile to be transferred in the gas phase and thermally stable at the reaction temperature. When the conditions of self-terminating surface reactions are fulfilled, only reactions between functional groups at the surface and the catalyst precursor occur.

The ALD technique is suitable for catalyst preparation using metal acetylacetonate precursors [37] (see also ref. 38 for a recent summary). It has been shown that the interaction mechanism between metal acetylacetonates and the support depends on the reactant–support pair and the experimental conditions.

1.2 Scope of the thesis

For a cobalt catalyst to be commercially viable for hydrogenation, e.g. the Fischer–Tropsch synthesis, the metal needs to be well dispersed, reducible and thermally stable. This can be achieved when the interaction between cobalt and support is strong enough to give a high dispersion, but weak enough to allow a significant extent of reduction. All stages of the catalyst preparation should be understood, therefore and optimised to obtain a catalyst with the desired properties.

This thesis summarises the results of the seven appended publications [I–VII]. The main part deals with Co/SiO_2 and Co/Al_2O_3 catalysts prepared by ALD with cobalt acetylacetonates, $Co(acac)_2$ and $Co(acac)_3$, as precursors [II–IV,VI,VII]. In addition, Co/SiO_2 catalysts prepared by gas phase adsorption of cobalt octacarbonyl [V] and by incipient wetness impregnation of cobalt nitrate [I,IV] have been studied.

The work was done with emphasis on the interaction between cobalt and the support and the effect of the interaction on dispersion and reducibility. The original goal was to test whether the ALD method could be used to prepare supported cobalt catalysts with high dispersion and active for hydrogenation. Accordingly, the suitability of cobalt acetylacetonate precursors, $Co(acac)_2$ and $Co(acac)_3$, for ALD processing was evaluated [II] and the interaction mechanisms of the precursors with the silica [II] and alumina [VII] supports was assessed. The effect of subsequent treatments on the distribution, nature and reducibility of the supported cobalt species was studied as well [II–IV,VI,VII]. The interest was not only in studying the cobalt–support interaction and the composition of the catalysts, but also the effect of the catalyst properties on chemisorption and catalytic activity. Hence, a number of samples was tested using gas phase hydrogenation of toluene as model reaction [I,III,IV,VI,VII]. An important application of aromatics hydrogenation is the production of high quality, aromatics free, diesel fuels. Aromatic compounds in diesel fuels increase undesired particle emissions. The observed reaction rates also provide a measure of the hydrogenation potential.

2 EXPERIMENTAL

2.1 Catalyst preparation

Two, in principle, different methods were applied for the preparation of supported cobalt catalysts: i) incipient wetness impregnation and ii) gas phase deposition techniques. The gas phase techniques included both atomic layer deposition (ALD) using cobalt acetylacetonate precursors and adsorption of cobalt carbonyl. The ALD catalysts were supplied by Microchemistry Ltd., a former subsidiary of Neste Oil Corp., and the carbonyl based samples by the University of Joensuu.

2.1.1 Atomic layer deposition

Both Co/SiO_2 and Co/Al_2O_3 catalysts were prepared in a flow-type ALD reactor by chemisorption of cobalt acetylacetonates, $Co(acac)_2$ [II,VI,VII] or $Co(acac)_3$ [II–IV,VI,VII], from the gas phase onto the support (Table 1). The precursors were evaporated at 170 or 180 °C, and the support was kept in a fixed bed at the same temperature. The precursor was passed through the support with nitrogen as carrier gas. The pressure in the reactor was kept at about 10 kPa.

The catalyst preparation by ALD consisted of the following subsequent steps: (a) preheating of the support, (b) chemisorption of the gaseous cobalt precursor up to surface saturation and (c) removal of the remaining ligands by calcination in synthetic air. Steps (b) and (c) were followed by a nitrogen purge. The cobalt content of the catalysts was increased by repeating steps (b) and (c).

Two sets of catalysts were prepared: one where the samples were calcined after each precursor deposition step (calcined catalysts), and another set where the last calcination step was omitted (uncalcined catalysts). A more detailed description of the catalyst preparation is given elsewhere [II,VII].

2.1.2 Adsorption of cobalt carbonyl

Some Co/SiO_2 samples were prepared by adsorption of $Co_2(CO)_8$ on SiO_2 fluidised in a flow of CO [V] (Table 1). The carbonyl precursor was evaporated into the CO flow at 35–45 °C, and the temperature of the fluidised bed was kept 5 °C higher. Some of the samples were decarbonylated at 100 °C in nitrogen. The cobalt loading on the samples was increased by repeating the deposition step after the decarbonylation step.

2.1.3 Incipient wetness impregnation

Co/SiO_2 catalysts were prepared by the incipient wetness impregnation technique using an aqueous solution of $Co(NO_3)_2$ [I,IV] (Table 1). The silica support was pretreated with a volumetric 1:1 ethanol–water solution and dried. The precursor, $Co(NO_3)_2 \cdot 6H_2O$, was dissolved in the pore volume amount of deionised water and added to the support. The catalyst was then dried under reduced pressure and calcined in synthetic air.

Table 1. Summary of the cobalt catalysts studied in the appended publications.

Sample	**Support**	**Precursor**	**Method**	**Publication**
Co(N,C) [a]	SiO_2	$Co(NO_3)_2$	Impregnation	I, IV
Co(A2,U)	SiO_2	$Co(acac)_2$	ALD	II
Co(A3,C) [a]	SiO_2	$Co(acac)_3$	ALD	II, III, IV, VI
Co(A3,U) [a]	SiO_2	$Co(acac)_3$	ALD	II, IV, VI
Co(C,U) [b]	SiO_2	$Co_2(CO)_8$	Gas phase adsorption	V
Co(C,D) [a,b]	SiO_2	$Co_2(CO)_8$	Gas phase adsorption	V
Co(A2,C) [a]	Al_2O_3	$Co(acac)_2$	ALD	VI, VII
Co(A2,U) [a,b]	Al_2O_3	$Co(acac)_2$	ALD	VI, VII
Co(A3,U) [b]	Al_2O_3	$Co(acac)_3$	ALD	VII

[a] metal loading varied

[b] support precalcination temperatures varied

2.2 Characterisation of the catalysts

A range of chemical and physical methods was used to study the cobalt species and their interaction with the support as a function of preparation conditions and cobalt content. Suitable ALD processing parameters for the cobalt acetylacetonate precursors ($Co(acac)_2$, $Co(acac)_3$) were determined by thermogravimetric studies (TG/DTG) and differential thermal analysis (DTA) [II]. The volatility and stability of the precursors were studied by heating in an inert atmosphere. The cobalt content of the catalysts was determined by atomic absorption spectrometry (AAS) [I–VII], inductively coupled plasma mass spectrometry (ICP-MS) [VI,VII] or instrumental neutron activation analysis (INAA) [II–IV,VI,VII]. The carbon content was measured with a carbon analyser [II,IV,VII], and the number of hydroxyl groups on the support was determined by ^{1}H MAS NMR.

The interaction of the cobalt precursors with silica and alumina was studied by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) [II,V,VII]. The distribution of cobalt through $Co(A3,C)/SiO_2$ catalyst particles were measured with a scanning electron microscope equipped with an energy dispersive spectrometer (SEM/EDS) [III]. The Co/SiO_2 catalysts were further studied by transmission electron microscopy (TEM) [III,IV] and the crystal structure of the cobalt species was determined by X-ray diffraction (XRD) [III].

The degree of reduction was estimated by X-ray photoelectron spectroscopy (XPS) [I,III,IV] or O_2-titration [III,IV,VI,VII]. The chemical shift in XPS was used to study the nature of the silica supported species [III]. The reducibility properties were also studied by temperature programmed reduction (TPR) [IV–VII], and the hydrogen consumption was measured with a thermal conductivity detector (TCD). In addition, a mass spectrometer was used for samples where the TCD signal did not represent hydrogen consumption.

The surface area (BET) and pore volume of the samples and supports were measured by nitrogen physisorption [II,III]. The hydrogen [I,III–VII] and CO [I,III,VII] chemisorption capacity measurements were performed by the static volumetric method on catalysts reduced in situ in flowing hydrogen. The total hydrogen uptake was used to estimate the dispersion and average particle size and the values were corrected for the degree of

reduction. Temperature programmed desorption (TPD) was also used to study the chemisorption of hydrogen on Co/SiO_2 and Co/Al_2O_3 catalysts [VI].

The activity of the $Co(N,C)/SiO_2$, $Co(A3,C)/SiO_2$, $Co(A3,U)/SiO_2$, $Co(A2,C)/Al_2O_3$ and $Co(A2,U)/Al_2O_3$ catalysts in gas phase toluene hydrogenation was evaluated using fixed bed reactors [I,III,IV,VI,VII]. The $Co(N,C)/SiO_2$, $Co(A3,C)/SiO_2$ and $Co(A3,U)/SiO_2$ samples were tested at 170 or 175 °C using a toluene to hydrogen ratio of 1:7. The composition of the gas was measured at the outlet of the reactor with an on-line FTIR analyser [I,III,IV]. Some of the $Co(A3,U)/SiO_2$, $Co(A2,C)/Al_2O_3$ and $Co(A2,U)/Al_2O_3$ catalysts were tested in a temperature programmed mode [VI,VII]. The reaction temperature was increased from 100 to 200 °C at a rate of 5 °C/min [VI] or from 30 to 150 °C at a rate of 1 °C/min [VII]. The toluene to hydrogen ratio was 1:12. The product stream was analysed with a mass spectrometer. The total hydrogen uptake was used to calculate turnover frequencies (TOF, s^{-1}).

3 RESULTS AND DISCUSSION

3.1 Precursor addition

3.1.1 Cobalt acetylacetonates

Fulfilling the conditions for self-terminating, i.e. saturating, gas–solid reactions in ALD requires that the processing temperatures be limited to an interval where the precursor chemisorbs on the support. The processing conditions may also be limited by the evaporation and decomposition temperatures of the precursor [37,38]. The conditions for ALD processing for the cobalt acetylacetonate precursors ($Co(acac)_2$, $Co(acac)_3$) were determined by thermoanalytical studies (TG/DTA) [II].

The TG curve measured for $Co(acac)_2$ showed some weight loss at 140–170 °C, probably due to release of water from hydrated complexes [39]. Major weight loss was seen starting at about 170 °C with a maximum at 225 °C, which was interpreted as evaporation of $Co(acac)_2$. Two intervals with major weight loss were observed for $Co(acac)_3$. The first starting from 180 °C with a maximum rate at 215 °C was interpreted as sublimation of $Co(acac)_3$. The second peak, at 235 °C, was assigned to evaporation of $Co(acac)_2$; that is, $Co(acac)_3$ undergoes thermolysis to form $Co(acac)_2$ at about 220 °C (reduction of Co^{3+} to Co^{2+}) [40,41].

Evaporation of $Co(acac)_2$ and $Co(acac)_3$ starts at about 170 and 180 °C, and to avoid decomposition the processing temperatures should be below 220 °C. Accordingly, 170 and 180 °C were used for catalyst preparation by ALD with $Co(acac)_2$ and $Co(acac)_3$ as precursors [II–IV,VI,VII].

One preparation cycle

One ALD preparation cycle consisted of adsorption of the $Co(acac)_2$ or $Co(acac)_3$ precursor on the support followed by calcination in air to remove the ligands [II–IV,VI,VII]. The majority of the samples were prepared on silica calcined at 600 °C [II–IV,VI] or alumina calcined at 875 °C [VI,VII], as summarised in Table 2.

Table 2. Summary of carbon and cobalt contents on $Co(acac)_2$ and $Co(acac)_3$ modified silica [II] and alumina [VII].

Support pretreatment (°C)	**Surface area**[a)] (m^2g^{-1})	**OH**[a)] (nm^{-2})	**Co** (wt.%)	**Co** (nm^{-2})	**C/Co**	**ligand/Co**	**ligand** (nm^{-2})
$Co(acac)_2/SiO_2$							
600	330	1.6	6.1	2.0	5.0	1.0	2.0
$Co(acac)_3/SiO_2$							
600	330	1.6	5.2	1.8	7.1	1.4	2.6
$Co(acac)_2/Al_2O_3$							
600	180	2.0	3.8	2.3	5.6	1.1	2.6
875	133	0.8	2.6	2.1	6.6	1.5	2.8
$Co(acac)_3/Al_2O_3$							
600	180	2.0	2.7	1.7	9.6	1.9	3.2
875	133	0.8	1.8	1.5	12	2.3	3.5

[a)] properties of the support

The cobalt content in wt.% after one preparation cycle was clearly higher on silica than on alumina (Table 2). The number of possible reaction sites, i.e. the OH surface concentration, was not found to limit the chemisorption of the precursor. Instead, the higher metal content on the silica sample was mostly due to the larger surface area, e.g., 330 m^2g^{-1} for 600-SiO_2 and 133 m^2g^{-1} for 875-Al_2O_3 with cobalt contents of 5.2 wt.% and 2.6 wt.%, respectively [II,IV,VII]. The corresponding packing densities were 1.8 and 2.1 nm^{-2}.

Evidently steric hindrance is a major factor in limiting the amount of cobalt precursor that can chemisorb on the support [II,VII]. A maximum acac ligand density of 2.2 nm^{-2} has also been found for chemisorption of $Ni(acac)_2$ on silica [42] and alumina [42,43], while the saturation density for $Cr(acac)_3$ on silica has been found to depend on the reaction conditions [44].

High loading samples

One ALD preparation cycle consisted of adsorption of the acac precursor followed by calcination in air to remove the ligands. The metal loading of the samples was increased by again reacting them with the precursor after the calcination step. The samples were kept in the ALD reactor during the whole preparation sequence. Catalysts, on both silica and alumina were prepared by applying one to five sequential chemisorption and air calcination steps on. This resulted in Co/SiO_2 and Co/Al_2O_3 catalysts with cobalt contents from about 5 to 20 wt.% and 3 to 10 wt.%, respectively [II–IV,VI,VII]. Expressed per surface area, the cobalt concentrations increased from about 2 to 8 Co nm^{-2} on both silica and alumina, with a clear correlation between cobalt loading and surface area (Figure 1).

The alumina supported catalysts were prepared with $Co(acac)_2$ to avoid possible competing chemisorption of the ligand released during the reduction of the $Co(acac)_3$ precursor [VII]. This is not a problem on silica because acetylacetone has not been observed to interact with silica between 200 and 220 °C [42,45].

Silica and alumina supported samples were also prepared by omitting the last calcination step; these samples are referred to in the text as 'uncalcined catalysts'.

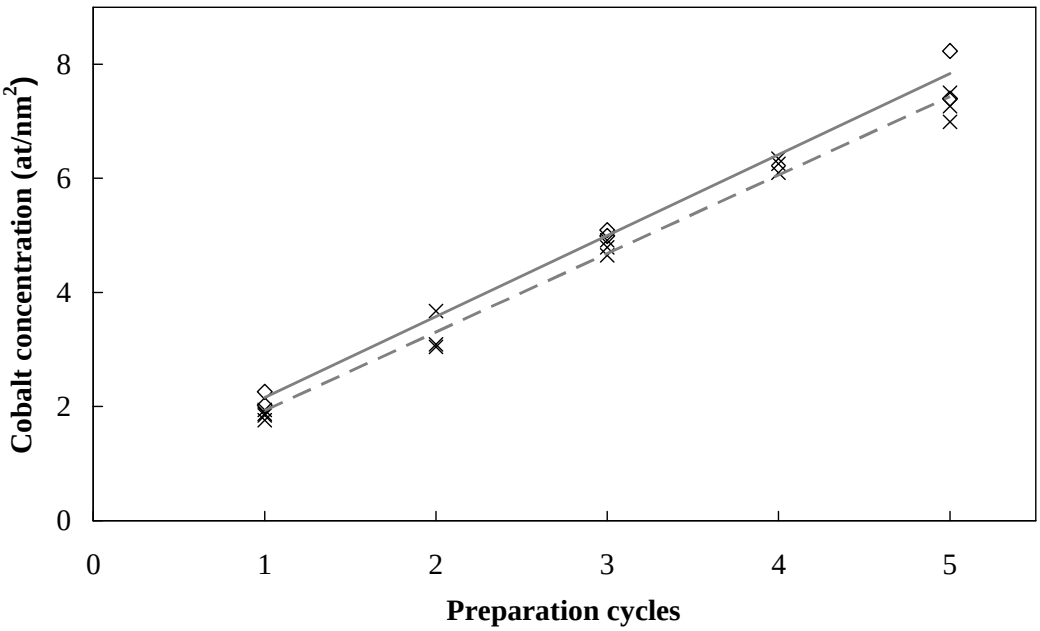

Figure 1. Cobalt concentration on 600-SiO_2 (crosses and broken line) and 875-Al_2O_3 (diamonds and continuous line) as a function of ALD preparation cycles [II–IV,VI,VII].

3.1.2 Cobalt carbonyl

Silica supported cobalt catalysts were also prepared in a fluidised bed with cobalt octacarbonyl ($Co_2(CO)_8$) as precursor [V]. The precursor was sublimated in a flow of CO and adsorbed on precalcined silica.

A surface saturation of about 2.5 wt.% Co was obtained independent of adsorption temperature (40–50 °C) or silica pretreatment temperature (300–600 °C). The concentration of OH groups on the silica support pretreated at 300–600 °C was estimated to be 3.6–1.5 nm^{-2}. Assuming that each $Co_2(CO)_8$ interacts with two OH groups, the cobalt concentration on the 600-SiO_2 support would have been 4.4 wt.% [V], i.e., the limiting factor for the saturation concentration was the size of the adsorbed species through steric hindrance.

The carbonyl species remained intact as long as the samples were kept under CO. The samples were decarbonylated in nitrogen at elevated temperatures (100–200 °C). Cobalt content was increased by repeating the adsorption step after the decarbonylation. Some samples that were used for TPR studies were not decarbonylated and were stored under CO.

3.1.3 Cobalt nitrate

The cobalt nitrate based catalysts were prepared by the incipient wetness impregnation technique. The desired amount of cobalt nitrate, $Co(NO_3)_2 \cdot 6H_2O$, was dissolved in the pore amount of water and added to the silica support in a single impregnation step [I,IV]. The samples were dried and then calcined in synthetic air at 300 °C to decompose the nitrate.

3.2 Interaction of cobalt precursor with the support

3.2.1 Cobalt acetylacetonates

Only a few studies have been published, in addition to those presented in this thesis, on catalyst preparation by ALD with cobalt acetylacetonates as precursors. Cobalt(III) acetylacetonate has been chemisorbed on zirconia [46–48] and on aluminium nitride modified silica [49].

The surface reactions that were considered for cobalt acetylacetonates on silica and alumina are given below in (1)–(5), where ▒ denotes the support surface. Ligand exchange reaction with OH groups [II,VII], reaction (1). Dissociative adsorption on coordinatively unsaturated Al-O pairs [VII], reaction (2). Associative adsorption either through hydrogen bonding, reaction (3a), or interaction with surface oxygen [50], reaction (3b), may have occurred to some extent on silica [II]. Reaction (3b) has previously also been observed for $Cr(acac)_3$ on silica [44]. Thermoanalytical studies [II] indicated that possible transformation of $Co(acac)_3$ to $Co(acac)_2$ reaction (4), may occur. As has been shown [42,45,51,VII] acetylacetone can react on alumina, reaction (5), analogously to reaction (2), whereas acetylacetone is not known to interact with silica [42,45].

$$\text{▒–OH} + Co(acac)_x\,(g) \rightarrow H(acac)\,(g) + \text{▒–O–}Co(acac)_{x-1} \quad (1)$$

$$\text{▒(AlO)} + Co(acac)_x\,(g) \rightarrow \text{▒Al(acac)} + \text{▒–O–}Co(acac)_{x-1} \quad (2)$$

$$\text{▒–OH} + Co(acac)_x\,(g) \rightarrow (Co(acac)_x)\cdots HO\text{–▒} \quad (3a)$$

$$\text{▒O} + Co(acac)_x\,(g) \rightarrow \text{▒O}\cdots(Co(acac)_x) \quad (3b)$$

$$Co(acac)_3\,(s \text{ or } g) \rightarrow Co(acac)_2\,(g) + \text{“acac”}\,(g) \quad (4)$$

$$\text{▒(AlO)} + H(acac)\,(g) \rightarrow \text{▒Al(acac)} + \text{▒–OH} \quad (5)$$

The DRIFT spectra of the bulk precursors [II,VII] (Figure 2 and Table 3), $Co(acac)_2$ and $Co(acac)_3$, showed absorption bands of the acac–ligands similar to reported values [52–56]. The characteristic lines of the ligand methyl groups at 3200–2800 cm^{-1} (Figure 2a) and the combined C=C and C=O stretching vibrations of the conjugated chelate ring system at about 1600–1580 and 1540–1520 cm^{-1} (Figure 2b, Table 3) were seen in the spectra of

silica and alumina modified with both precursors [II,VII]. The lines were also seen in the spectra of the H(acac) modified alumina (Figure 2b and Table 3) [VII]. The conclusion that can be drawn from the DRIFTS measurements is that the acac–ligands remained intact on both silica and alumina after the adsorption [II,VII].

Table 3. Summary of DRIFTS data for bulk compounds and reacted alumina and silica samples [II,VII].

	[n(C=C) + n(C=O)]	**[n(C=O) + n(C=C)]**	**(acac)-Al**	**(acac)-Co**
$Co(acac)_2$ bulk				
[VII]	1588	1519		1261
[52,54–56]	1601–1588	1521–1513		1270–1255
$Co(acac)_3$ bulk				
[VII]	1591	1535		1279
[52,53,55]	1587–1568	1538–1520		1284–1274
$Al(acac)_3$ bulk				
[52,53,56]	1590–1585	1530–1523	1291–1280	
Alumina samples [VII]				
$Co(acac)_2/600\text{-}Al_2O_3$	1594	1520	1289	1262
$Co(acac)_2/875\text{-}Al_2O_3$	1594	1521	1292	1263
$Co(acac)_3/600\text{-}Al_2O_3$	1592	1523	1291	1263
$Co(acac)_3/875\text{-}Al_2O_3$	1593	1525	1292	1263
$H(acac)/600\text{-}Al_2O_3$	1593–1589	1531	1296	
Silica samples [II]				
$Co(acac)_3/600\text{-}SiO_2$	1585	1522		

The band observed between 1296 and 1261 cm^{-1} (Table 3) is sensitive to the central metal ion [51,57]. In this region the spectra of the alumina supported samples resembled more closely those of bulk $Co(acac)_2$ than $Co(acac)_3$ (Figure 2). Furthermore, the DRIFT spectra of $Co(acac)_3/SiO_2$ resembled more the spectra of bulk $Co(acac)_2$ than $Co(acac)_3$ in the region of the combined C=C and C=O stretching vibrations of the conjugated chelate ring sample [II].

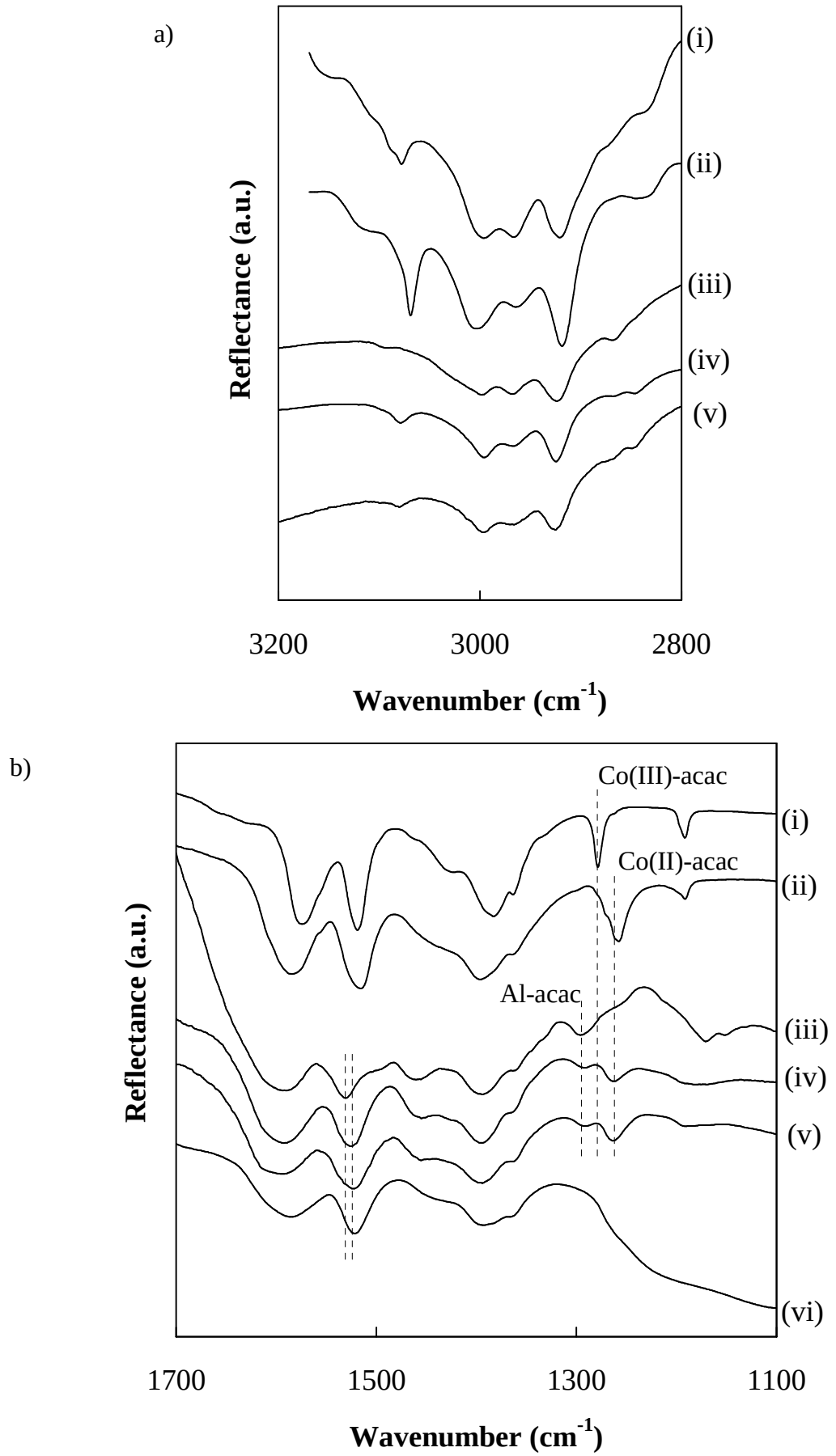

Figure 2. DRIFT spectra of (i) bulk $Co(acac)_3$, (ii) bulk $Co(acac)_2$, (iii) $H(acac)/Al_2O_3$, (iv) $Co(acac)_2/Al_2O_3$, (v) $Co(acac)_3/Al_2O_3$, (vi) $Co(acac)_3/SiO_2$ [II,VII].

In the spectrum of the H(acac) modified alumina, a band was seen at 1296 cm^{-1}, which corresponds to values reported for $Al(acac)_3$ [52,53,56]. The band was also seen on cobalt acetylacetonate modified alumina independent of the precursor and pretreatment temperature (600/875 °C). This indicated the presence of $Al(acac)_x$ species, which could be taken as evidence of the dissociation reaction (5) on alumina [VII].

The C/Co ratios of the samples were studied and compared with the stoichiometry of the above reactions (1)–(5). Since the presence of intact ligands was shown by the DRIFT spectra [II,VII], it was also justified to calculate ligand densities. The ligand/Co ratio on silica [II] was close to one for both $Co(acac)_2$ and $Co(acac)_3$ (Table 2). A weak increase in the ligand/Co ratio with pretreatment temperature was seen for $Co(acac)_3$ on silica. On the other hand, there was a clear difference in the ligand/Co ratio between the precursors on alumina, the ratio with $Co(acac)_3$ was close to 2, while the ratio for $Co(acac)_2$ was about one (Table 2). The ligand/Co ratio for both $Co(acac)_2$ and $Co(acac)_3$ on alumina increased with pretreatment temperature [VII].

The DRIFT spectra indicated that the cobalt species on the supports were similarly independent of the precursor. This, together with the C/Co ratio on silica suggested that $Co(acac)_3$ transformed to $Co(acac)_2$, according to reaction (4), before bonding to the support [II]. The carbon balance on silica indicated that the main mode of interaction for both precursors was ligand exchange (6). Associative adsorption also occurred to some extent as shown by the Co/OH and C/Co ratios (3b) [II]. There was no interference of the ligand released in reaction (1) because acetylacetone does not interact with silica.

$$\text{▒–OH} + Co(acac)_2\,(g) \rightarrow H(acac)\,(g) + \text{▒–O–}Co(acac) \qquad (6)$$

The interaction on alumina was more complex because of dissociative adsorption on coordinatively unsaturated Al-O pairs. Starting with $Co(acac)_2$, the ligand/Co ratio (Table 2) indicated that the main chemisorption mode is the ligand exchange reaction (6), which is the only reaction that will give a ratio of 1. The observed increase in the C/Co ratio with pretreatment temperature indicates that a fraction of the precursor adsorbed dissociatively (7) and/or that released ligands adsorbed dissociatively (5). The Al-acac species seen in the DRIFT spectra suggested that dissociative reaction on coordinatively unsaturated alumina

sites occurred (Figure 2). The higher than unity Co/OH ratios also indicate other interaction in addition to the ligand exchange reaction.

$$\equiv(AlO) + Co(acac)_2\,(g) \rightarrow \equiv Al(acac) + \equiv\!-O\!-Co(acac) \qquad (7)$$

Dissociative adsorption of the ligand released in reaction (4) probably affected the C/Co ratio when $Co(acac)_3$ was used with alumina. Otherwise the interaction mechanism is the same as for $Co(acac)_2$. The carbon content showed ligand concentrations on the modified silica samples and the $Co(acac)_2$ modified alumina sample to be between 2.0 and 3.5 nm^{-2} (Table 2). From on the estimated size of the acac–ligand, the maximum concentration after one reaction cycle should be between about 2.2 and 3.4 acac/nm^2 [II]. This further supports the assumption that the maximum obtainable ligand concentration, i.e., steric hindrance, determined the saturation level.

To increase the cobalt loading, the samples were calcined and the reaction cycle was repeated [II,VII]. The increase in cobalt per cycle per unit surface area (nm^{-2}) on the high loading samples was nearly constant and independent of the support material (Figure 2), which further showed steric hindrance as the limiting factor.

The C/Co ratio of the last precursor addition step on the high loading samples, i.e., 2 to 5 chemisorption cycles on the basis of the nearly linear increase of cobalt: the C/Co ratio was on average 4.5 on silica [II] and 9.2 on alumina [VII]. This corresponds to ligand/Co ratios of 0.9 and 1.8, which indicate that the main mode of interaction on silica was the ligand exchange reaction, while on alumina both ligand exchange and dissociative adsorption occurred. The ligand surface concentration was close to what was observed for the one-cycle sample, about 2.5 on silica and 2.8 on alumina, again indicating surface saturation control by steric hindrance.

3.2.2 Cobalt octacarbonyl

Cobalt octacarbonyl, $Co_2(CO)_8$, was adsorbed on silica samples partially dehydroxylated at 300, 500 and 600 °C. A decrease in the intensity and broadening of the isolated silanol band in the DRIFT spectra during deposition of $Co_2(CO)_8$ indicated adsorption through hydrogen bonding. It was concluded that hydrogen bonding occurs between weakly acidic surface hydroxyls and the oxygen of bridging CO groups [V].

The concentration of free OH groups on silica after vacuum treatment at 300, 500 and 600 °C has been estimated to be 3.6, 1.8 and 1.5 nm^{-2}, respectively [V]. Thus, the maximum amount of cobalt on silica precalcined at 600 °C would be 4.4 wt.% if every $Co_2(CO)_8$ molecule bonds to two OH groups. However, the cobalt content was about 2.5 wt.% on all samples independent of the number of bonding sites; in other words, the cobalt content was not determined by the number of OH groups but was limited by steric hindrance [V].

The IR spectra showed that the molecular structure of the adsorbed carbonyl was $Co_4(CO)_{12}$ [V], which is a dimerisation product of $Co_2(CO)_8$. Furthermore, the amount of CO released during H_2-TPR of non-decarbonylated samples corresponded to a CO/Co ratio of 3 [V], which is the same ratio as for $Co_4(CO)_{12}$.

Decarbonylation of the adsorbed carbonyl species was done under nitrogen at elevated temperatures (100–200 °C). Higher metal loading was achieved through repetition of the deposition–decarbonylation cycles. According to the IR spectra the mode of adsorption did not change during the following adsorption cycles. This was supported by the observed linear increase in cobalt content with adsorption cycles [V].

3.2.3 Cobalt nitrate

The interaction of the cobalt nitrate precursor with the support was not studied in detail in the appended publications. After the impregnation the samples were dried and then calcined at 300 or 500 °C to decompose the nitrate salt and produce Co_3O_4 on the surface [I].

3.3 Reducibility of the cobalt species

A catalytically active material can be efficiently used by dispersing it on a stable, high surface area oxide, such as silica or alumina. The reducibility of a supported catalyst will depend on the interaction of the dispersed species with the support. The interaction should be strong enough to give a well dispersed thermally stable catalyst but weak enough to allow high reducibility. In general, silica is considered to be a support that results in weaker interaction than alumina [e.g. 1,2,58].

3.3.1 Extent of reduction

An experimental correction factor [59,60] was used together with the $Co^0/Co2p_{3/2}$ peak area ratios to determine the extent of reduction of the $Co(N,C)/SiO_2$ samples [I]. The degree of reduction on the $Co(N,C)/SiO_2$ catalysts was found to be high. The extent of reduction for a 4.6-$Co(N,C)/SiO_2$ catalyst increased from 60 to 84% with reduction temperature over the interval 300–400 °C, while a decrease to 70% was observed after reduction at 450 °C. The decrease was attributed to agglomeration of cobalt particles, which affects the surface sensitive XPS method. Silicate formation and migration of silica could not be excluded, although XPS and TPR showed no evidence of cobalt silicate (section 3.3.2) [IV]. In comparison, the degrees of reduction (400 °C) of two samples containing 4.6 and 13 wt.% Co, determined by O_2 titration, were 84 and 87% [IV]. These values agree well with the ones obtained by XPS [I].

The $Co(A3,C)/SiO_2$ samples required significantly higher reduction temperatures than the $Co(N,C)/SiO_2$ ones. The degrees of reduction of $Co(A3,C)/SiO_2$ samples reduced at 550 °C were estimated by XPS, and found to be less than 30% even for a sample containing 19 wt.% Co [III]. O_2-titration measurements showed higher degrees of reduction, between 50 and 60% (Table 4) [VI], but even these levels of reduction can be considered low taking into account the high reduction temperature (550 °C/7 h). The XPS method probably underestimated the amount of metallic cobalt [61,I], owing to the surface sensitivity of the method.

The $Co2p_{3/2}$ to Si2p peak area ratio of a calcined 13.4-$Co(A3,C)/SiO_2$ was compared with that of a corresponding reduced sample (550 °C/7 h). The ratio was 2.9 times as high on

the calcined sample as on the reduced sample. The lower ratio seen for the reduced sample indicated that sintering had occurred during the high temperature reduction [III]. However, it could also have been due to migration of silica, which could cause the cobalt particle to be partly covered by silica [62,63].

Calcination decreased the reducibility of the Co/SiO_2 ALD catalysts, especially at low loadings. Oxygen titration measurements showed that the degree of reduction of the uncalcined $Co(A3,U)/SiO_2$ catalysts after reduction at 550 °C was between 52 and 63% independent of the cobalt loading [IV]. The degree of reduction on these catalysts was comparable to that of the $Co(A3,C)/SiO_2$ catalysts, except at low cobalt loading where the calcination significantly decreased the reducibility (Table 4).

Calcination also decreased the reducibility of the alumina supported catalysts [VI,VII]. The degree of reduction of uncalcined samples was, in general, higher than that of the corresponding calcined ones, but the difference decreased with increasing loading.

3.3.2 Cobalt surface species on silica

The TPR measurement of a catalyst prepared by incipient wetness impregnation of cobalt nitrate (4.6 wt.% Co) showed a two-step reduction profile (Figure 3) [IV]. The area of the peak at 300 °C was about one third of the peak at 350 °C. This two-stage pattern is typical for the reduction of Co_3O_4 via CoO to Co [16,63,64]. The TPR spectrum showed no hydrogen consumption above 500 °C, thus suggesting that no cobalt silicates were present. The TPR spectrum was in line with the high degree of reduction observed for the $Co(N,C)/SiO_2$ catalysts, i.e., after calcination the major part of the cobalt was present as Co_3O_4. The easily reducible catalysts indicated a weak interaction between the cobalt species with the support and modest dispersion.

As shown by the TPR spectra, the species on the $Co(A3,C)/SiO_2$ catalysts were very different from the Co_3O_4 phase on the cobalt nitrate based samples [IV,VI,VII]. Hydrogen consumption was mainly seen above 700 °C, and only for high loadings (ca. 20 wt.%) was a small peak seen at 330 °C indicating that some Co_3O_4 had formed. The hydrogen consumption above 700 °C was attributed to cobalt silicates or hydrosilicates [8,65]. It was

concluded that calcination of the Si-O-Co(acac) surface species formed during preparation produced silicate-like species [III].

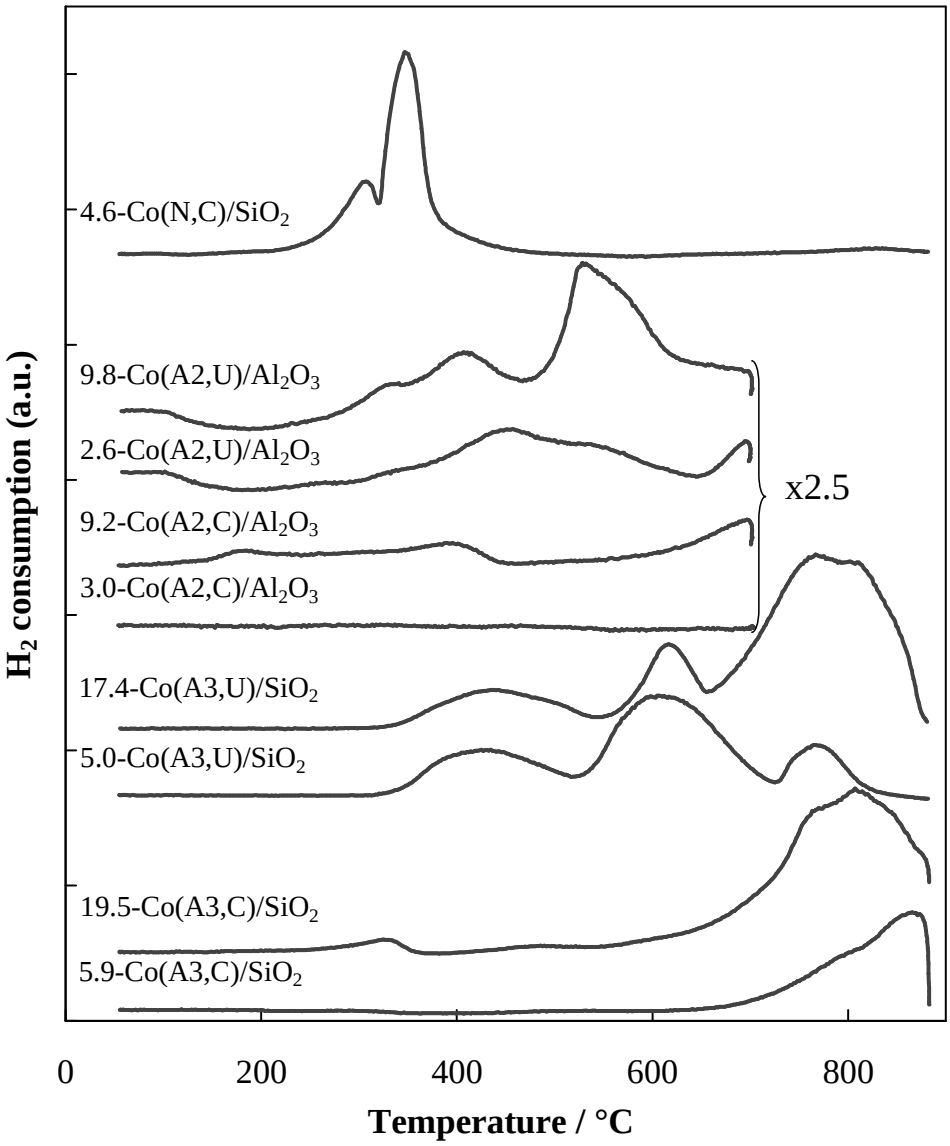

Figure 3. TPR spectra of $Co(N,C)/SiO_2$, $Co(A2,U)/Al_2O_3$, $Co(A2,C)/Al_2O_3$ $Co(A3,U)/SiO_2$ and $Co(A3,C)/SiO_2$ catalysts [IV,VI,VII].

Further confirmation of the presence of cobalt silicate on the $Co(A3,C)/SiO_2$ samples was obtained by studying the Co $2p_{3/2}$ feature in the XP spectra [III]. Comparison was made with the reference spectra of Co_3O_4 and Co_2SiO_4. The peak at about 778.3 eV in the XP spectra of the reduced samples was ascribed to metallic cobalt. The shake-up satellite features on the high binding energy side of the metallic peak suggested that Co^{2+} was present on the surface [66]. The position of the metallic peak remained constant for all the

samples, while the binding energies of the non-metallic peaks decreased with metal loading. The peak shift was interpreted as a chemical shift due to an increased amount of silicate on the surface [11,67,68,III]. The relative amount of silicate was larger on the low loading samples, in agreement with TPR results and the low degrees of reduction.

In addition, XRD measurements of a calcined 19.0-Co(A3,C)/SiO_2 sample indicated the presence of Co_3O_4 and/or Co_2SiO_4, but no definitive conclusion could be drawn from the diffractograms due to weak and overlapping reflections [III].

The reducibility of the Co/SiO_2 ALD samples was improved when the final calcination step was omitted, so that some of the silicate formation was avoided. However, also the uncalcined one cycle ALD sample, 5.0-Co(A,U)/SiO_2, showed some species that reduced at 750 °C (Figure 3) indicating formation of some CoO_x-SiO_2 species during the TPR measurement [63,IV].

Three broad peaks, at 400, 600 and 750 °C, were seen in the TPR spectra of the Co(A3,U)/SiO_2 samples (Figure 3). The evolution of acetone, which is formed when the acetylacetonate ligands decompose, was observed at 350-400 °C, and mainly methane and other light hydrocarbons above 500 °C [IV] due to the hydrogenation of carbonaceous species. Water appeared mainly at the first and third hydrogen consumption peaks. The water that formed above 700 °C was likely due to reduction of silicates.

3.3.3 Cobalt surface species on alumina

The TPR profile of the calcined one-cycle 3.0-Co(A2,C)/Al_2O_3 sample [VI] showed practically no hydrogen consumption between 50 and 700 °C (Figure 3) and indicated the presence of a ‘fully’ dispersed cobalt oxide in a strong interaction with the alumina [2]. The hydrogen consumption below 450 °C on catalysts with higher metal loading was attributed to Co_3O_4 reducing to CoO [16,69] and at higher temperatures further to Co. The species reducing above 600 °C are likely to be very strongly interacting CoO [16] and cobalt aluminate type compounds [14,70]. Aluminate-type species can be formed by migration of cobalt into the alumina lattice [11,14]. The peak below 200 °C might be due

to some residual carbonaceous material from the precursor since no cobalt species are expected to reduce at these temperatures.

The TPR spectra of the Co(A2,U)/Al_2O_3 samples [VI] showed a more complex pattern due to the carbonaceous species remaining from the precursors than the corresponding calcined catalysts. During the TPR of the five-cycle 9.8-Co(A2,U)/Al_2O_3 sample, acetone was observed between 320 and 370 °C as a result of decomposition of the acetylacetonate ligands. Hydrogenation of carbonaceous residues was seen as the formation of methane with a maximum at 530 °C, and of other light hydrocarbons (C_2 and C_3) between 320 and 450 °C. Water was mainly observed above 550 °C probably due to the reduction of cobalt oxides and/or aluminates. Even in the TPR spectrum of the one-cycle 2.6-Co(A2,U)/Al_2O_3 sample there were some species that reduced above 650 °C. It has been suggested that cobalt diffuses into the support during reduction (TPR) [64], and this could account for the high temperature reduction peak in the uncalcined one-cycle sample.

In summary, calcination decreased the reducibility of both silica and alumina supported ALD catalysts prepared from cobalt acetylacetonate precursors. The highly dispersed Si-O-$Co(acac)_x$ and Al-O-$Co(acac)_x$ species formed during the preparation of the catalysts are probable precursors for the cobalt silicate and aluminate-type compounds that formed during calcination [II-IV,VI,VII].

3.4 Dispersion of cobalt

The chemisorption of a probe molecule offers a useful way to measure the surface area and dispersion of metal on a supported catalyst. Where the chemisorption stoichiometry is known, the monolayer capacity gives the number of metallic surface atoms. The monolayer capacity can then be used to calculate the dispersion, i.e., the ratio of surface metal atoms to the total number of metal atoms. Assuming e.g. spherical particles the average particle diameter can be obtained. Knowledge of the number of surface atoms is also useful for catalyst activity testing, i.e., for calculation of the TOF. On the assumption that the metallic cobalt is in a separate phase, the dispersion and particle size can be corrected for the degree of reduction [I].

3.4.1 Hydrogen chemisorption

A representative monolayer capacity of hydrogen can be difficult to obtain on cobalt owing to activated chemisorption [58,71–74,I,III,VI]. The activation has been found to depend on the properties of the sample, i.e., the interaction between the support and the metal [58,71–73]. In addition, the reversibility of hydrogen chemisorption has been found to depend on the metal support interaction [73].

The effect of the chemisorption temperature was studied on nitrate based Co(N,C)/SiO_2 catalysts [I]. The total uptake of hydrogen increased when the measurement temperature was increased from 30 to 100 °C. The observed activation factors, here defined as the ratio of uptake at 100 °C to uptake at 30 °C, were 1.1, 1.1 and 1.4 for catalyst samples reduced at 300, 400 and 500 °C, respectively. The activation factors were in agreement with published values [58]. The activation factor increased with reduction temperature, i.e., with increasing cobalt–support interaction.

The chemisorption capacity of Co(A3,C)/SiO_2 catalysts reduced at 550 °C was also measured at 30 and 100 °C [III]. Again the hydrogen uptake increased with measurement temperature. The activation factor varied from 1.05 to 1.46 but did not show any clear trend as a function of metal loading.

The reversibility of the hydrogen chemisorption was estimated by measuring a second isotherm after 40 min of outgassing following the measurement of the total chemisorption isotherm. A correlation was observed between the fraction of weakly chemisorbed hydrogen and the properties of the sample. The weakly chemisorbed fraction was higher on samples with small uptakes, i.e., low cobalt surface areas [VI]. However, the outgassing procedure might be more effective on samples with low uptakes. The measurement temperature also had an effect on the reversible amount and, as expected, reversibility increased with temperature. The chemisorption of hydrogen was less reversible at 100 °C on the Co/Al_2O_3 than on the Co/SiO_2 ALD catalysts [VI].

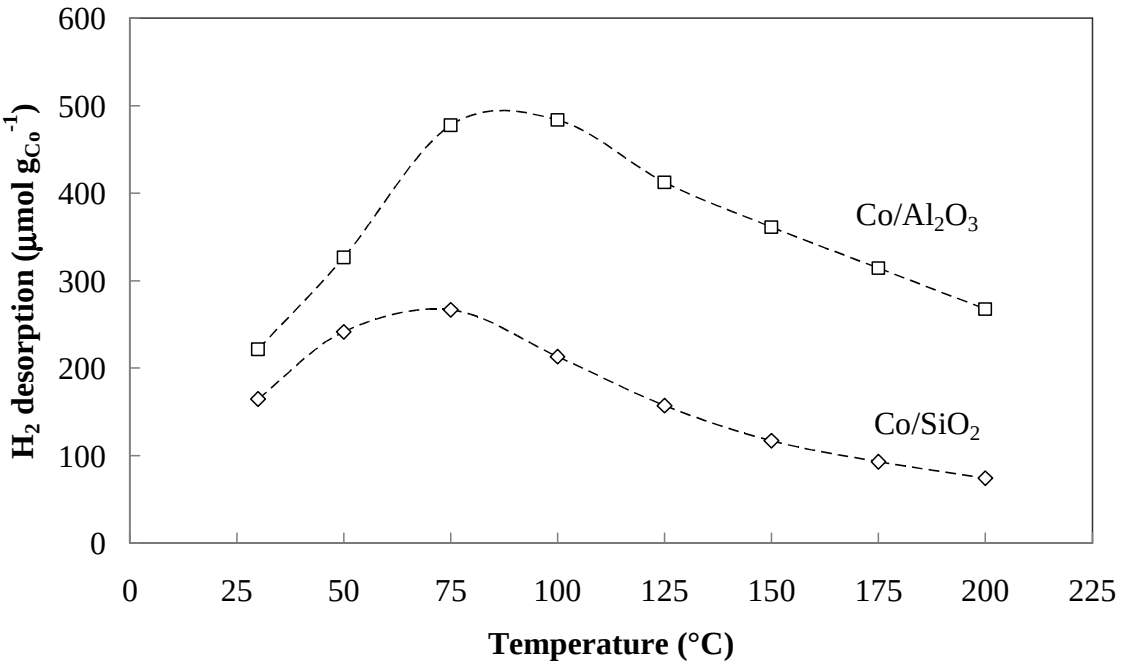

Figure 4. Amount of desorbed hydrogen as a function of adsorption temperature on a 15.9-Co(A3,U)/SiO_2 and a 9.8-Co(A2,U)/Al_2O_3 sample, measured by TPD [VI].

The 15.9-Co(A3,U)/SiO_2 and 9.8-Co(A2,U)/Al_2O_3 samples reduced at 550 °C were exposed to hydrogen at several temperatures between 30 and 200 °C followed by TPD [VI]. The amount of hydrogen that chemisorbed onto the catalysts was found to depend on the chemisorption temperature (Figure 4). On the 15.9-Co(A3,U)/SiO_2 sample, the maximum uptake was obtained at 75 °C and on the 9.8-Co(A2,U)/Al_2O_3 sample at 100 °C.

At least three different adsorption states were observed on the 15.9-Co(A3,U)/SiO_2 sample seen in the TPD spectra as desorption at 50–100, 100–170 and 170–300 °C. Similar

desorption peaks were observed in the spectra of the 9.8-Co(A2,U)/Al_2O_3 sample except for the slightly higher desorption temperatures [VI]. The desorption peak maxima occurred at 180 °C for the 9.8-Co(A2,U)/Al_2O_3 sample and at 130 °C for the 15.9-Co(A3,U)/SiO_2 sample. Hydrogen seemed to be more strongly chemisorbed on the 9.8-Co(A2,U)/Al_2O_3 than on the 15.9-Co(A3,U)/SiO_2 sample, which is in line with the lower reversibility observed on the alumina supported catalyst in the static measurements [VI]. The activation factors, here defined as the ratio of uptake at 100 °C to uptake at 30 °C, measured by TPD were higher than those observed by static measurements on the same samples. The activation factors for the 15.9-Co(A3,U)/SiO_2 and 9.8-Co(A2,U)/Al_2O_3 catalyst were 1.62 at 75 °C and 2.19 at 100 °C [VI]. The corresponding factors for static measurements were 1.0 and 1.1 [VI]. Higher activation factors for TPD than for static measurements have also been reported by Zowtiak et al. [71,72].

The results from the hydrogen chemisorption studies underline the importance of using a correct chemisorption temperature to obtain full surface coverage. The majority of the H_2-chemisorption measurements in the appended publications were obtained at 100 °C [I,III–VII]. Since the activation factors were fairly low for static measurements, the measurement at 30 °C can still be used at least for comparison. The effect of the adsorption temperature is more important in TPD measurements as shown by the high activation factors. However, the highly reversible chemisorption of hydrogen on cobalt also led to low surface coverage in the TPD measurements.

3.4.2 CO chemisorption

The interpretation is not as straightforward for the CO chemisorption measurements as for hydrogen because the stoichiometry varies with the type of adsorbed CO species (linear, bridged and polycarbonyls) [24,75]. The adsorption stoichiometry has been reported to vary with support and metal loading [24,73]. Furthermore, CO also adsorbs on unreduced cobalt species [76].

On the Co(N,C)/SiO_2 catalysts, a significant drop was seen in hydrogen chemisorption capacity with increasing reduction temperature [I,IV]. The adsorption of CO was less sensitive to the reduction temperature, but after reduction at 500 °C the CO chemisorption

capacity also decreased significantly. The CO/H ratio increased with reduction temperature, indicating chemisorption on non-metallic species. Reduction temperatures above 450 °C probably caused sintering [I]. Migration of silica probably also reduced the available cobalt surface area [62,63]

The chemisorption of CO at 30 °C was also measured on Co(A3,C)/SiO_2 [III], Co(A2,C)/Al_2O_3 and Co(A2,U)/Al_2O_3 [VII] samples. The total CO uptake on the reduced silica supported samples containing 5.9 to 19.5 wt.-% Co was nearly independent of the cobalt loading. On the reduced alumina supported samples, the total CO chemisorption followed the trends seen in the hydrogen chemisorption; that is, the CO chemisorption capacity generally increased with the loading and it was higher on the uncalcined samples than on the calcined ones. The CO/H ratio decreased with increasing cobalt loading on both silica and alumina supported samples. Adsorption of CO on non-metallic species [75,76] was probably the reason for the observed high total CO chemisorption capacity at low loadings. The chemisorption of CO on non-metallic species is highly reversible, however [III,VII]. The fraction of irreversibly chemisorbed CO on the reduced samples increased with loading, i.e., with the surface area of metallic cobalt.

Hydrogen was concluded to be a better probe molecule than CO for estimating the metal surface area of supported cobalt catalysts so long as the activated chemisorption is taken into account. The chemisorption of CO can, however be useful when studying the activity and selectivity properties of catalysts for CO hydrogenation.

3.4.3 Dispersion based on hydrogen uptake

The reducibility and chemisorption measurements revealed significant differences in the surface species of the catalysts. The hydrogen uptake on the Co(N,C)/SiO_2 catalysts reached a maximum after reduction at 300 °C [I,IV]. Reduction above 400 °C resulted in a severe decrease in the hydrogen chemisorption capacity probably due to agglomeration [I,IV] and possibly due to migration of silica [62,63]. Increasing the calcination temperature from 300 to 500 °C likewise decreased the hydrogen uptake, implying sintering of the cobalt particles [I]. The dispersion ranged between 4 and 8% on the studied Co(N,C)/SiO_2 samples depending on the reduction temperature [I].

The $Co(A3,C)/SiO_2$ catalysts behaved in a remarkably different way from the $Co(N,C)/SiO_2$ catalysts. A maximum hydrogen uptake was reached after reduction at 550 °C for all cobalt loadings (6–20 wt.%) [III,IV]. Reduction at temperatures below 500 °C gave negligible hydrogen uptake. The hydrogen uptake increased with cobalt content but remained modest even on the 19.5 wt.% catalyst. The uptakes on the $Co(A3,C)/SiO_2$ catalysts were also low in comparison with those on the $Co(N,C)/SiO_2$ catalysts (Table 4), mostly due to the low reducibility.

The dispersion of the $Co(A3,C)/SiO_2$ samples decreased with increasing cobalt content (Table 4, Figure 5). The dispersion on the low loading samples was high (19-29%); however, the values are uncertain due to the very low uptake and degree of reduction. The high reduction temperatures that were needed probably caused sintering and/or migration of silica as seen from the XPS spectra where the $Co2p_{3/2}$ to Si2p peak intensity ratio decreased significantly during the reduction at 550 °C [III].

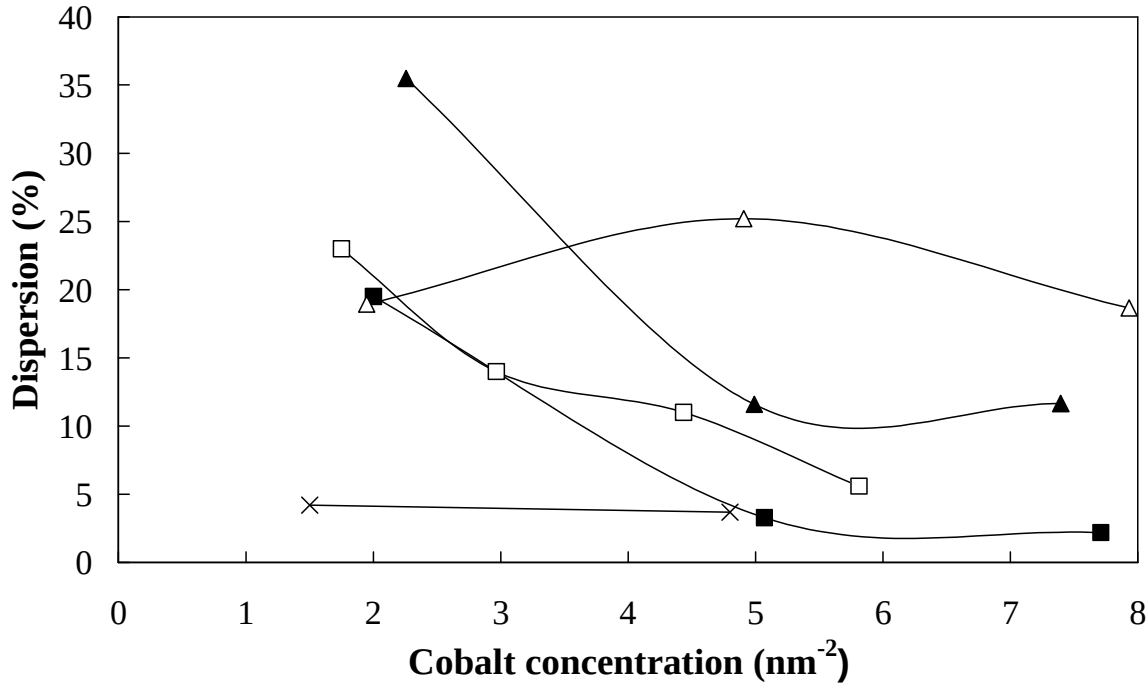

Figure 5. Dispersion as a function of cobalt surface density [I,III,VI–VIII]. The ALD samples were reduced at 550 °C and the nitrate based samples at 400 °C. × $Co(N,C)/SiO_2$, ■ $Co(A3,C)/SiO_2$, □ $Co(A3,U)/SiO_2$, ▲ $Co(A2,C)/Al_2O_3$ and Δ $Co(A2,U)/Al_2O_3$.

Table 4. Hydrogen uptake, degree of reduction (f), dispersion (D) and particle size (d) of Co/SiO_2 and Co/Al_2O_3 catalysts [I,III–VII]. Data for selected reduction temperatures are shown.

Sample		**Reduction temperature** (°C)	**H_2-uptake at 100 °C** ($\mu mol/g_{sample}$)	**f** (%)	**D** (%)	**d** (nm)
4.6-Co(N,C)/SiO_2	[I, IV]	400	13.9	84 [b]	4.2	23
12.6-Co(N,C)/SiO_2	[IV]	400	34.7	87	3.7	26
2.2-Co(C,U)/300-SiO_2	[V]	400	16.9 [a]			
2.3-Co(C,U)/300-SiO_2	[V]	400	12.5 [a]			
5.7-Co(A3,C)/SiO_2	[III]	550	5.7	4 [c]	29	4.1
5.9-Co(A3,C)/SiO_2	[III, VI]	550	11.7	12 [c]	19	4.9
13.4-Co(A3,C)/SiO_2	[III]	550	11.1	23 [c]	4.3	23
13.7-Co(A3,C)/SiO_2	[III, VI]	550	19.2	50	3.3	29
19.0-Co(A3,C)/SiO_2	[III]	550	17.4	28 [c]	3.8	25
19.5-Co(A3,C)/SiO_2	[III]	550	23.2	64	2.2	44
5.2-Co(A3,U)/SiO_2	[IV, VI]	550	52.0 [a]	52	23	4.2
8.5-Co(A3,U)/SiO_2	[IV, VI]	550	65.3 [a]	63	14	6.7
12.2-Co(A3,U)/SiO_2	[IV, VI]	550	62.1 [a]	54	11	8.7
15.4-Co(A3,U)/SiO_2	[IV, VI]	550	46.1 [a]	63	5.6	17
3.0-Co(A2,C)/Al_2O_3	[VI]	550	4.2	5	35.5	2.7
6.4-Co(A2,C)/Al_2O_3	[VI]	550	25.6	41	11.6	8.3
9.2-Co(A2,C)/Al_2O_3	[VI]	550	54.2	60	11.7	8.3
2.6-Co(A2,U)/Al_2O_3	[VI]	550	5.1	12	19.0	5.1
6.3-Co(A2,U)/Al_2O_3	[VI]	550	75.9	56	25.4	3.8
9.8-Co(A2,U)/Al_2O_3	[VI]	550	105	68	18.5	5.2

[a] measured at 30 °C

[b] determined by XPS, correction factor applied [I]

[c] determined by XPS

The maximum hydrogen uptake occurred at much higher reduction temperatures on the ALD catalysts, than on the Co(N,C)/SiO_2 catalysts. The high reduction temperatures were probably due to the high dispersion of the precursor, causing strong interaction between the cobalt species and the support.

The hydrogen uptake increased significantly when the last calcination step was omitted (uncalcined ALD catalysts). High reduction temperatures were still needed, however; the maximum hydrogen uptake on the Co(A3,U)/SiO_2 samples was obtained after reduction at 500 to 550 °C. On the one-cycle Co(A3,U)/SiO_2 samples, the difference was dramatic: the hydrogen chemisorption capacity increased up to six times. The increase at higher cobalt concentrations was less profound but still significant (Table 4). The explanation for the improvement was in the different degrees of reduction of these catalysts. The uncalcined species might have an effect analogous to the addition of a promoter, which has been found to increase both the degree of reduction and the dispersion [e.g. 77]. The difference in reducibility between calcined and uncalcined catalysts was most profound for the samples with lowest cobalt content. On both calcined and uncalcined ALD Co/SiO_2 catalysts, the dispersion decreased with increasing cobalt loading.

Two Co(A3,C)/SiO_2 samples (13 and 19 wt.%) were studied by XRD spectroscopy in order to determine the sizes of the crystalline cobalt phases [III]. However, these could not be determined due to weak and partly overlapping peaks. The particle sizes obtained from the chemisorption measurements for similar samples are considerably larger than suggested by the weak XRD patterns [III], which means that the cobalt particles probably consist of weakly ordered species. It is also possible that the cobalt species are present as a two-dimensional surface silicate [14], which would be difficult to detect by XRD.

The dispersion was higher on the alumina supported catalysts than on similar silica supported samples with the same surface concentration of cobalt (Figure 5). The dispersions were especially high on the uncalcined Co(A2,U)/Al_2O_3 catalysts. A maximum was observed in the hydrogen uptake as a function of reduction temperature at 550 °C on the Co(A2,C)/Al_2O_3 catalysts and at 600 °C on the Co(A2,U)/Al_2O_3 ones [VII]. However, the highest dispersion was obtained after reduction at about 500–550 °C. The uncalcined

sample was also less susceptible to sintering at reduction temperatures between 450 and 650 °C.

The carbonyl based samples [V] showed relatively high hydrogen uptakes, i.e., high metal surface areas, despite the low loadings (Table 4, reduction at 400 °C). As cobalt is zerovalent in the carbonyl precursor, there is a potential to produce catalysts with high degrees of reduction. The TPR measurements of these samples also suggested high degrees of reduction by 400 °C [V].

3.5 Catalytic activity

Gas phase hydrogenation of toluene was used to test the catalytic activity of some of the cobalt catalyst samples described in the appended publications [I,III,IV,VI,VII]. Relatively few studies have been published on the hydrogenation of aromatics on cobalt [62,78–84]. On the basis of literature it is unclear whether the hydrogenation of aromatics on cobalt is structure sensitive. The TOF of benzene hydrogenation on cobalt has been reported to be independent of the support material (silica, silica–alumina or alumina) and particle size [78]. However, in the hydrogenation of benzene on Ni, Rh, Pd and Pt at low temperatures (25–120 °C) the TOF has been indicated to depend on the particle size for particles smaller than 20 nm [85].

The effect of reduction temperature on the activity of a 4.6-Co(N,C)/SiO_2 catalyst in toluene hydrogenation was studied for catalysts reduced at 200–500 °C [I]. The reaction rate reached a maximum after reduction at 200–300 °C, while reduction at 500 °C resulted in almost inactive catalysts due to the loss of metallic cobalt area through sintering or migration of silica [I]. The reaction rate correlated with the hydrogen uptake, i.e., the surface area of metallic cobalt.

Similar Co(N,C)/SiO_2 samples as described in this thesis have also been tested in CO hydrogenation [I,60]. The conversion in CO hydrogenation on a 4.6-(N,C)/SiO_2 catalyst was found to increase with cobalt surface area [I]. This result is in line with studies showing that the rate of CO hydrogenation on cobalt catalysts is proportional to the metal surface area [23,29].

In the case of the Co(A3,C)/SiO_2 samples, reduction at 400 °C was not sufficient to activate the catalysts, and reduction at 500 °C gave only slightly active catalysts. The activity of the Co(A3,C)/SiO_2 catalysts was therefore tested after reduction at 550 °C, which was the temperature that gave the maximum hydrogen uptake [III]. The hydrogenation activity of the Co(A3,C)/SiO_2 samples increased with metal loading but remained modest for all cobalt contents. In contrast, the reaction rate on the corresponding Co(A3,U)/SiO_2 catalysts, reduced at 550 °C, was about one order of magnitude higher than that on the Co(A3,C)/SiO_2 samples.

The reaction rate per exposed cobalt, or TOF, was calculated from the hydrogen uptake data [III,VI]. The TOF values of the Co(A3,C)/SiO_2 and Co(N,C)/SiO_2 catalysts were roughly the same, while the TOF values of the Co(A3,U)/SiO_2 were about two to three times higher. However, the large differences in the reaction rates and conversion levels made the interpretation uncertain. In general, it seemed that the surface area of reduced cobalt is the most important factor for the activity in the reaction; i.e., toluene hydrogenation on cobalt is a structure insensitive reaction.

Some of the Co(A3,U)/SiO_2 samples have also been tested in hydroformylation of ethene [86]. In ethene hydroformylation the oxo-selectivity, which describes the CO insertion activity, increased with dispersion [86]. The well dispersed Co(A3,U)/SiO_2 catalysts were found to be promising catalysts for ethene hydroformylation in terms of both selectivity and stability [86].

Toluene hydrogenation activity tests were also performed, for both silica and alumina supported ALD catalysts, in a transient or temperature programmed mode [VI,VII]. A reaction rate maximum was found at ca. 105±10 °C for all tested samples regardless of the support or metal loading. The differences observed in the activation of hydrogen chemisorption did not influence the reaction rate maximum significantly. The reaction rate on the different catalysts showed large variations. The difference was mainly due to the different surface areas of metallic cobalt. The TOF calculated at the temperature of maximum reaction rate did not show a dependence of TOF on the particle size [VI,VII].

The decrease in the reaction rate with increasing reaction temperature (>110 °C) is probably related to the surface coverage of hydrogen [VI,VII]. It was seen from the TPD spectra that the surface coverage of hydrogen on the catalysts decreases rapidly above 100 °C. After each reaction run, the samples were flushed with an 11 vol.% H_2/Ar mixture before cooling. During the cooling in the H_2/Ar mixture, a desorption peak of toluene and methylcyclohexane was observed between 170 and 130 °C, which indicates that hydrocarbons were present on the surface even at 200 °C. Hence, the low reaction rate at high temperatures would be due to an insufficient surface coverage of hydrogen.

No evidence of structure sensitivity was found for toluene hydrogenation on cobalt [I,III,IV,VI,VII]. However, the conversion levels varied significantly for the different samples, which made the interpretation of the results uncertain. A particle size effect can not, therefore, be excluded.

4 SUMMARY

A primary goal of this work was to investigate whether atomic layer deposition (ALD) with cobalt acetylacetonate precursors can offer a practical way to produce a highly dispersed reducible cobalt catalyst. A related aim was to gain understanding on how different precursors and thermal treatments affect the interaction between the support and the cobalt species. Further, the effect of the precursors and treatments on the properties of the catalysts, i.e., the reducibility and dispersion, was of interest as well as how these affect catalyst performance.

Silica supported cobalt catalysts were prepared by incipient wetness impregnation method using cobalt nitrate as precursor. The weak interaction between the cobalt species and silica on catalysts prepared by incipient wetness impregnation led to high reducibility but a modest dispersion. The main cobalt species on the calcined nitrate based catalysts was Co_3O_4. The extent of reduction increased with reduction temperature. However, the use of reduction temperatures above 400 °C decreased the available metal surface area significantly, probably due to sintering of cobalt and migration of silica; that is, the thermal stability of the catalysts was low.

Co/SiO_2 samples were also prepared by adsorption of $Co_2(CO)_8$ from the gas phase. The $Co_2(CO)_8$ precursor interacted through weak hydrogen bonding with silanol groups on the silica. Rearrangement of $Co_2(CO)_8$ to $Co_4(CO)_{12}$ on the silica was observed. Subsequent heat treatment at elevated temperatures (100–150 °C) led to complete decarbonylation. The saturation level on the silica surface was controlled by steric hindrance.

The cobalt acetylacetonate precursors ($Co(acac)_3$, $Co(acac)_2$) were found suitable for catalyst preparation by ALD, and surface saturation was achieved. Regardless of support and pretreatment, the factor limiting the cobalt loading was steric hindrance. Silica supported cobalt catalysts were prepared by ALD using $Co(acac)_3$. The precursor $Co(acac)_3$ transformed to $Co(acac)_2$, before reacting through a ligand exchange reaction with the OH groups of the silica. Associative adsorption of $Co(acac)_2$ probably occurred to some extent on silica. Alumina supported cobalt catalysts were prepared by ALD using $Co(acac)_2$. The interaction of the $Co(acac)_2$ precursor with alumina was proposed to

proceed both via a ligand exchange reaction with OH groups and via dissociative adsorption. The cobalt loading was increased by repeating the precursor addition and air calcination steps up to five times. This procedure gave samples with 5–20 wt.% Co on silica and 3–10 wt.% Co on alumina, on both supports the amount of cobalt per unit surface increased from about 2 to 8 Co atoms per nm^2.

Calcination of the silica supported ALD samples produced silicate-type CoO_x-SiO_2 species that are hard to reduce. Low degrees of reduction resulted, even at high temperatures (550 °C). The reducibility and metal surface area of the Co/SiO_2 catalysts increased when the last calcination step was omitted. Similarly, calcination of $Co(acac)_2$ modified alumina produced aluminate-type compounds or a surface oxide layer interacting strongly with the support. On samples with cobalt contents above 3 wt.%, however, a significant part of the cobalt was present as reducible species. The maximum metal surface area was obtained at high reduction temperatures (500–600 °C). Again the metal surface area was higher on the uncalcined catalysts. The dispersion of cobalt on the alumina supported catalysts was higher than on the silica supported ones, being especially high on the uncalcined alumina supported catalysts.

The chemisorption of hydrogen on supported cobalt was shown to be activated and highly reversible. The hydrogen chemisorption measured by TPD at the temperature of maximum uptake compared with the uptake at 30 °C was higher by factors of 1.6 and 2.2 for cobalt on silica and alumina, respectively. In general, activation factors obtained by static measurements were lower, from 1.0 to 1.5.

Wide variations were observed in the reaction rate of toluene hydrogenation on the cobalt catalysts. In general, the activity correlated with the cobalt surface area. Differences were also seen in the TOF, though no proof of a particle size effect could be shown.

The alumina supported ALD catalysts, especially the uncalcined samples, showed high dispersions and reasonable degrees of reduction. These samples could prove useful when used as catalysts for a structure sensitive reaction. A significant drawback of the ALD cobalt catalysts is the high reduction temperatures that are required. The ALD samples would benefit from further study perhaps with a promoter used to enhance the reducibility.

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